INSTRUMENTATION AND TECHNIQUES

The development of new techniques and instrumentation goes hand in hand with the continuing scientific advances at any state of the art facility. The NSLS is no exception. Because of its unique infrastructure these developments are advanced on many fronts by the entire community. As in past years significant innovations are being made over the entire photon energy spectrum covered by the NSLS facility.

Developments in UV and Soft X-Ray Instrumentation

A new area of focus for UV photoemission studies is in the realm of very high energy and momentum resolution. These techniques have been applied to questions of interest in the field of high T_c superconductors over the past several years. As part of the push in that direction at NSLS, a new high energy resolution angle-resolving photoemission instrument based on the use of a Scienta hemispherical analyzer has recently been commissioned in the BNL Physics Department. This spectrometer, with the capability of multiplexing in both energy and angle, has an energy resolution of better than 5 meV and an angular resolution of better than 0.2 degrees, resulting in an order of magnitude improvement of the momentum resolution. It is intended to couple this instrument to the new undulator beamline U13UB, which features high throughput collection/focusing optics and a high resolution ($> 10^4$ resolving power) normal incidence monochromator operating in the 5 to 30 eV photon energy range.

Imaging science using soft x-rays is now well established. The instrumentation, however, continues to develop as experimenters push ever harder toward the physical resolution limit of $\lambda/2$. The X1A scanning x-ray microscopes all use Fresnel zone plates as their focusing elements. In collaboration with D. Tennant (Lucent Technologies Bell Laboratories), S. Spector *et al.* (SUNY @ Stony Brook), have fabricated zone plates by etching Ge or, more recently, plating Ni. Outer zone widths of 30 nm are in use, and 20 nm zones have been fabricated in tests; diameters of 80 and 160 microns are in use.

The Stony Brook team has not only made advances in the x-ray optics but have also commissioned a scanning transmission x-ray microscope, cryo-STXM, which is designed (by J. Maser, *et al.* SUNY @ Stony Brook,) to image frozen hydrated specimens of a few microns in thickness at temperatures below -165°C. At this temperature, the effects of radiation damage to biological samples should be reduced by several orders of magnitude compared to room temperature hydrated specimens. This should enable images to be taken at higher resolution and even multiple images to be obtained from the same sample, a feature which is crucial for elemental and chemical mapping and for tomography. In contrast to most x-ray microscopes in use, the cryo-STXM has been designed to operate at a vacuum of 10^{-7} Torr. This limits thermal drifts to around 1 nm per second while also helping to reduce contamination of the sample. Samples are prepared on EM grids which in turn are mounted on a TEM style liquid nitrogen cooled holder. The sample temperature can be controlled by a heater. The holder itself can tilt by ± 80° to allow tomography to be done. Sample introduction is done through a JEOL TEM airlock, and takes only a few minutes without breaking vacuum. Images are obtained by scanning the sample in a raster pattern, the x-ray light being focused at a fixed point using a Fresnel zone plate. Coarse scans with a resolution of 1 micrometer are performed by out-of-vacuum stepping motors with a range of 9 mm by 25 mm. A piezo driven in-vacuum flexure stage provides finer steps of 20 nm and a field of 70 by 70 μm^2. Refocusing during spectral scans is done using an in-vacuum DC motor. Samples can be previewed using an optical microscope with infinity-corrected visible light lenses in vacuum but with the head outside vacuum. The data acquisition system has multiple digital and analog channels so that several parameters can be recorded. The cryo-STXM is now permanently mounted on a separate vibration isolation system at the beamline.

Scanning transmission x-ray microscopy provides a two dimensional image of the sample under study. Holographic techniques hold out the promise of providing information about the third dimension. Previous experiments in x-ray holography have yielded high quality images of dried specimens at ~40 nm resolution. These experiments have employed the photoresist PMMA for recording the image, a specialized scanning force microscope with a linear scanning stage for hologram readout, and computer reconstruction. In 1996, the experimental apparatus was completely rebuilt (by S. Lindaas (LBNL), and collaborators from Stony Brook) to allow holograms to be recorded of frozen hydrated specimens using a cryo holder similar to that which is used in cryo-STXM. First holograms of frozen hydrated malarial erythrocytes were recorded, and reconstructions have been obtained at a resolution similar to that of room temperature samples. Moreover, iterative twin image elimination algorithms have been developed for higher quality image reconstruction. Plans for 1997 include efforts towards holographic tomography.

X-Ray Methods and Instrumentation

High Pressure Research

The high pressure tools that are used in conjunction with the NSLS source have undergone major advances as reported in this volume. The variables: magnitude, uniformity, and isotropy of pressure, magnitude and uniformity of temperature, and sample volume all compete in defining the envelope available to the researcher. The diamond anvil cell sets the high pressure limit at the price of sample volume, and pressure and temperature uniformity. The "double hot plate" system used by T.-D. Shen *et al.* (Los Alamos National Laboratory), in their study of iron defines new boundaries in this experimental space. Two multi-mode laser beams are focused on opposite faces of the sample through the opposed diamond anvils. By heating both surfaces of the sample to the same temperature, the normally large temperature gradients within the sample are virtually eliminated. Using Kirkpatrick-Baez mirrors, the x-ray beam is focused to a diameter of about 10 μm, providing sufficient intensity for diffraction spectra to be collected in a few minutes. This spot size is much smaller than the laser spot size, thus, providing x-ray data for a sample at uniform pressures and temperatures.

"Large volume" high pressure systems define the portion of the experimental envelope with sample volumes three orders of magnitude greater than diamond anvil cells with a sacrifice in maximum pressure and a gain in pressure and temperature homogeneity as well as sample volume for x-ray studies. The new anvil geometry reported by M. Vaughan *et al.* (SUNY @ Stony Brook), the Tea-Cup cell [Figure 54(a) and (b)], is beginning to compete with diamond anvil cell pressures having broken 21 GPa with tungsten carbide anvils while maintaining large sample volumes. Future plans include using sintered diamonds as anvils with the hope of further increasing pressure with little loss of other parameters; cost.

The conventional large volume system used at X17 is a DIA style multi-anvil apparatus. This workhorse at NSLS and the Photon Factory (where it is known as MAX-80 and MAX-90) can routinely produce 10 GPa with WC anvils with a 4 mm truncation. Wang *et al.* (U. of Chicago) report slight modifications to the anvil geometry that have provided a 30% increase in pressure, fewer failures, and more productive experimental runs, all

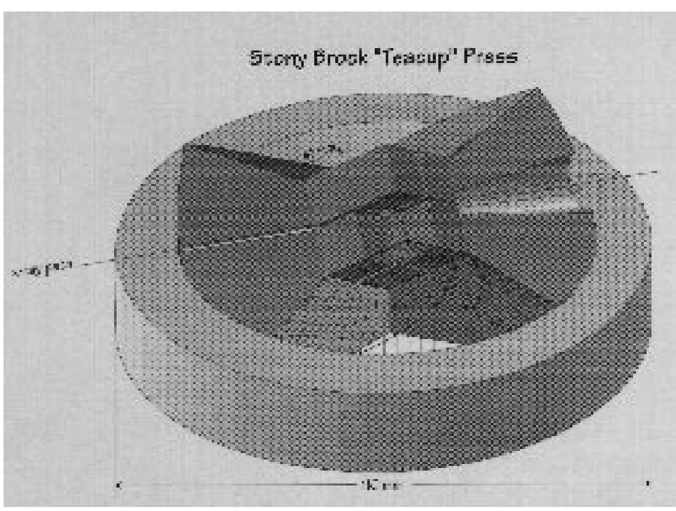
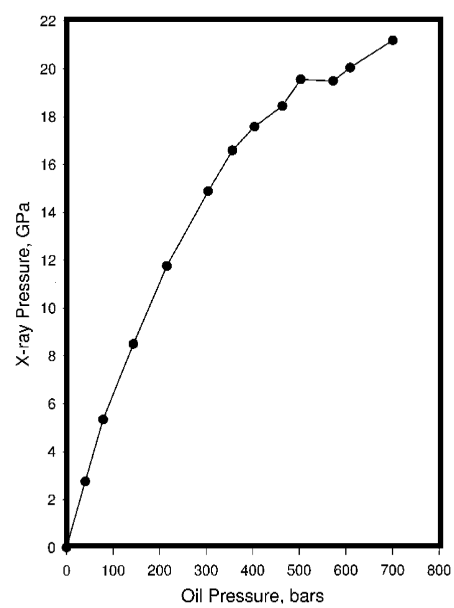


Figure 54: (a) Stony Brook "Teacup" Press, a two-stage device using eight-cubic anvils to generate high pressure, with x-ray access. (X17B1)



(b) Pressure performance of Teacup apparatus.

with no cost in sample size or environment.

With the expansion of the experimental environmental envelope has come a remarkable growth in the types of studies that can be done in conjunction with x-ray synchrotron radiation. The most significant breakthrough for Earth-related studies is the inclusion of acoustic velocity measurements at high pressure and temperature and simultaneously with x-ray diffraction. As reported by R. Liebermann *et al.* (SUNY @ Stony Brook), acoustic interferometry is used to measure acoustic velocities of samples to fractions of a per cent accuracy (see Figure 55 for diagram of cell assembly). X-rays are essential to provide *in situ* determinations of the pressure using a NaCl pressure marker, with thermocouples measuring temperature. These experiments are all performed in the tapered anvil DIA apparatus, reproducing conditions of the transition zone of the Earth. Such measurements at simultaneously high pressure and temperature are extremely important in interpreting seismic velocities as a function of depth in the Earth. Despite their inherent importance, such measurements have been limited to a few samples, most notably, MgO, collected a quarter century ago. The MgO data reported here by G. Chen *et al.* (SUNY @ Stony Brook), using the new technology, cover a pressure range one order of magnitude larger than the older data with temperatures of twice the previous study.

H.-K. Mao *et al.* (Carnegie Institute of Washington), have developed a technique to estimate elastic anisotropy and strength at room temperature and megabar pressure in a diamond anvil cell. Experimentally, the cell geometry must be altered so that the x-rays enter and exit through the gasket and not the diamonds. Energy dispersive spectra are collected at varying diffraction directions, ranging from nearly parallel to the diamond axis to perpendicular to it. With assumptions as to the orientation and homogeneity of the deviatoric stress field, they can recover information about the elastic anisotropy and material strength. Their new results for iron have exciting implications about the elastic anisotropy and evolution of the Earth's inner core.

Macromolecular Crystallography

Multilayer monochromators can provide x-ray intensities from NSLS x-ray bending magnet beam lines that surpass currently available intensities from NSLS x-ray wiggler beam lines which use silicon monochromators. Using beam line X25, collaborators S. Burley and J. Kuriyan (Howard Hughes Medical Institute and Rockefeller U.), and L. Berman, M. Capel, and R. Sweet (Brookhaven National Laboratory), employed broad bandwidth multilayers (with a relative wavelength spread of 1.5%) as monochromating elements instead of

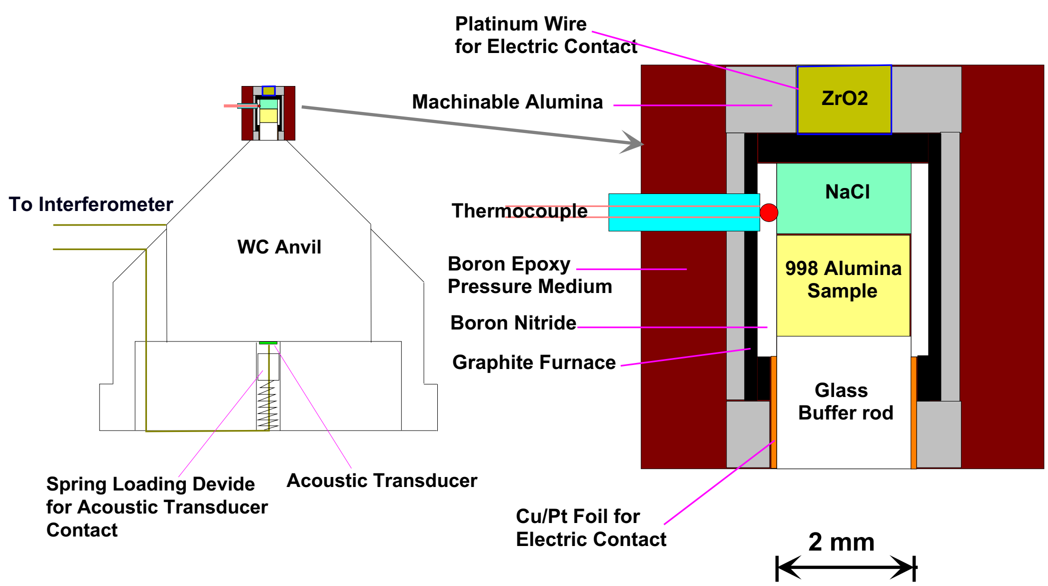


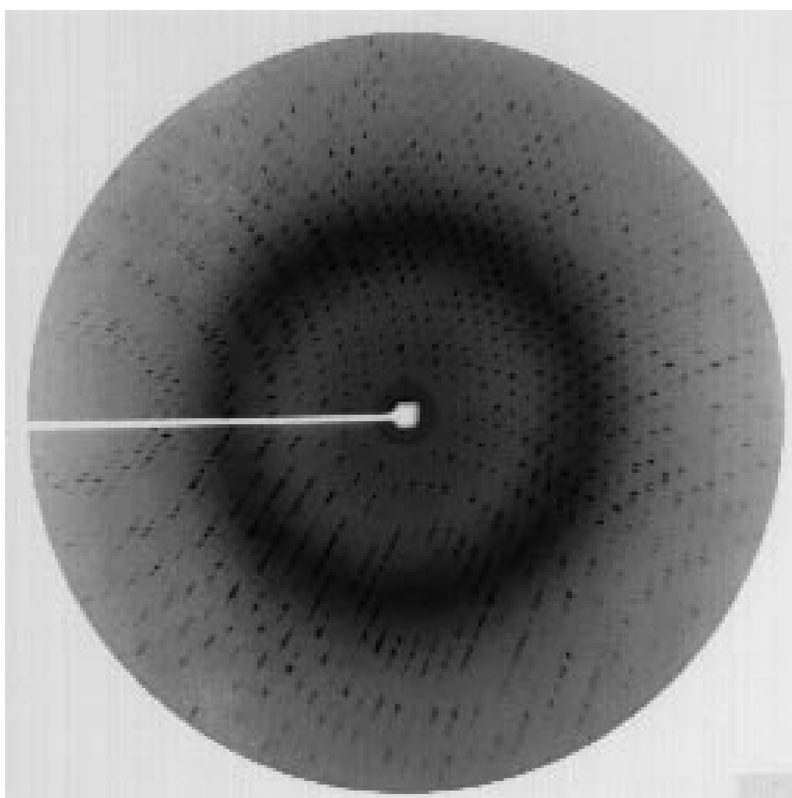
Figure 55: Diagram of anvil insert and cell assembly for ultrasonic experiments in X17Bl.

conventional narrow bandwidth silicon, in trial macromolecular crystallography experiments. The multilayers provide an additional two orders of magnitude of flux in the incident x-ray beam. Diffraction data were measured from two test specimens: single crystals of hen egg-white lysozyme and of TAFIA, a heterodimer of two eukaryotic transcription factors (Figure 56). These are being analyzed to determine how well the Bragg spots can be resolved and indexed, and their structure factors extracted, in the presence of the peculiar, highly anisotropic resolution function associated with the multilayer-monochromated x-ray beam. These tests at X25 were performed under single-bunch operation conditions, for which the x-ray intensity approximates that available on bending magnet stations under normal 25-bunch operation conditions. Nonetheless, exposure times were surprisingly short, ranging from one to five seconds for a 1° oscillation, and pushed the technical limits of the data collection apparatus' shutter cycle and phi axis rotation. Certain classes of crystallography problems should be solvable using such an x-ray beam. The major restriction is that the ratio of the smallest Bragg spacing resolution attainable to the longest crystallographic axis repeat is limited by the relative bandwidth of the x-ray beam from the multilayer monochromator. Within this limitation, the dramatic intensity enhancement derived (compared with the use of a silicon monochromator) should make possible high-resolution studies of weakly diffracting crystals on NSLS x-ray bending magnet beam lines, that are now impossible to execute there.

Advances have been made in crystallographic data collection. J. Skinner and R. Sweet (Brookhaven National Laboratory) have been developing, on beamline X12C, beamline-control software that incorporates intelligence and experience into a user-friendly graphical interface to the experimental apparatus. They operate a "hybrid" instrument that combines a commercial kappa-axis goniometer and interchangeable x-ray area imaging detectors. The software provides the user with a simple graphical user interface (GUI) to control both the diffraction equipment and the beamline (e.g. wavelength changes and alignment). Important features of the software are that it allows "one-button" operation of many functions that are actually quite complex, and provides automatic documentation of the experiment by writing log files to describe the operations that are performed, and others that contain data about them.

For example, the software facilitates the measurement of diffraction data for MAD phasing of macromolecular structures. Following a simple table set

Figure 56: Single diffraction pattern of crystal of hen egg-white lysozyme collected with a multilayer monochromator. (X25)



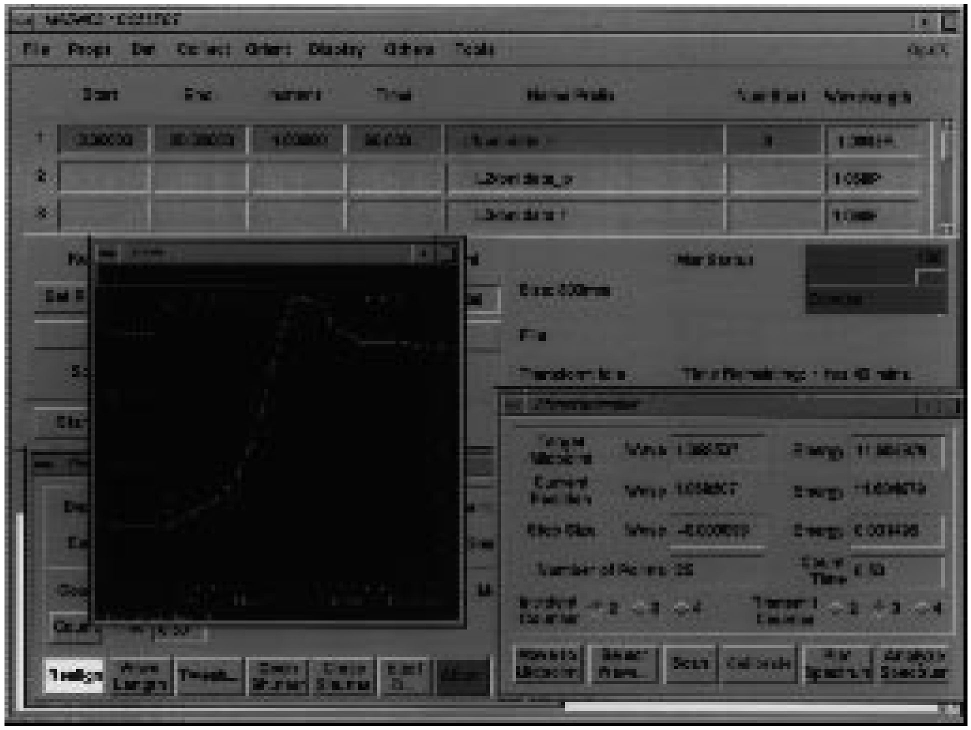


Figure 57: Beamline control software with a sample of an EXAFS scan. (X12C)

up by the operator to describe the experiment, the software will measure the x-ray absorption spectrum of the heavy atom incorporated in the crystal, analyze that spectrum to locate a particular feature at which data should be collected (e.g. the inflection point of the absorption edge), and then collect diffraction data at that wavelength (Figure 57). Numerous “ordinary” MAD structures have been solved with the system. Recently, a 1000-residue protein structure with over a dozen heavy (Se) atoms was solved. A small protein structure also was solved during single-bunch running, just 54 hours after the users commenced data collection and while they were still at the beam line collecting data on other problems.

Diffraction Physics

A recurrent issue in x-ray diffraction is the phase problem. Although it is not generally an obstacle in conventional crystallography, there are still areas where the answer is not overdetermined and interference phenomena can be helpful in retrieving the phase Information. An interesting attempt to provide phase information in a 2-D diffraction experiment was made by Y. Yacoby *et al.* (Hebrew U.). They were able to use an adsorbed gold layer to reflect the diffracted wave back into the sample in a surface-diffraction geometry, and to show that additional interferences resulted. These interferences may prove helpful in assigning reflection phases and hence determining structures.

Techniques for focusing and guiding x-ray continue to be pursued throughout the x-ray scientific community. C. Liu and J. Golovchenko (X15A, Harvard U.) have successfully observed the propagation of surface-trapped x-ray waves along the surface of a curved silicon mirror. The wave undergoes successive total external reflections on the surface, and its evanescent tail is simultaneously diffracted by the substrate lattice. The phenomenon may have important applications for x-ray optical elements such as lenses and waveguides.